

A NEW SOLUTION-BASED COAL-UPGRADING PROCESS

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INTRODUCTION

The development of effective means of upgrading the organic part of coal by separating it from the inorganic part has long been the goal of coal chemists and engineers, with several processes having been studied in recent years. Amongst these are the removal of mineral components by hot-alkali dissolution [1,2], the removal of minerals and some organic sulphur by treatment with perchloroethylene [3], and the high-severity extraction of the organics by coal-derived and supercritical solvents [4]. Relatively milder extraction with refluxing N-methyl-pyrrolidone (NMP) has also enjoyed attention [5], although the degree of solubilization obtained has been less than 50%. The aim of these studies has been to develop processes suitable for the manufacture of clean fuels or, after carbonization, of electrode carbons. The low value of these products places great pressure on the economics of the process.

The development of a new purification process has been prompted by the observation that relatively small additions of sodium hydroxide allow very high solubilization of certain high-rank bituminous coals into relatively cheap N,N-dimethylformamide (DMF) and similar solvents. A patent has been granted in South Africa [6], allowed in the USA and applied for in a number of other countries. The purified dissolved organics may be recovered from solution as "Refcoal" but the coal solution itself may be exploited to prepare products of much greater value than fuel or electrodes.

EXPERIMENTAL

Small-scale extractions

The extractions were performed at room temperature in stainless-steel tubes (80 ml volume) fitted with screw caps and PTFE seals. Typically coal (7 g), solvent (70 g) and alkali were introduced together with a stainless-steel slug (1 cm by 1 cm diameter). Air was displaced by nitrogen and the tubes sealed. Up to 12 tubes were placed in a tumbling apparatus and rotated end-over-end at 60 r/min for 24 hours at room temperature. The extract was filtered through No. 3 sintered-glass filter, washed once with solvent (70 g), then exhaustively with water to remove residual solvent and dried under vacuum at 60 °C. The residue was weighed, the carbon content determined and the degree of carbon extraction calculated using the formula:

$$\% \text{ Carbon extraction} = \frac{(\text{wt coal extr.} \times \% \text{ C in coal} - \text{wt extr. residue} \times \% \text{ C in residue}) \times 100}{\text{wt. coal extr.} \times \% \text{ C in coal}}$$

The repeatability, particularly for high degrees of extraction, was high. The figures shown are averages of at least two determinations.

Bench-scale extractions

The extraction apparatus consisted of a jacketed stainless-steel reactor 240 mm x 81 mm i.d., fitted with internal baffles and a flat stirrer 40 x 40 mm driven by a variable-speed motor capable of 1 500 r/min. The extractions were conducted under an argon atmosphere. Oil or water from a thermostat was pumped through the jacket to provide temperature control. The reactor was

loaded with coal (70 g) and solvent (700 ml) and heated to operating temperature. Alkali was added and the extraction commenced. Samples of slurry were taken as required and the degree of extraction measured.

Monitoring the degree of extraction

Slurry samples (≈ 1 ml) were centrifuged at 3 000 r/min for 5 minutes, then 0,1 g of supernatant was weighed rapidly into a volumetric flask and diluted to 50 ml with solvent. The absorbance at 600 nm was measured on a Unicam SP 1700 spectrophotometer.

Minerals removal

Extracts were centrifuged at 6 000 r/min for 30 minutes in 1- ℓ buckets and the supernatant filtered under vacuum through polypropylene filter cloth. The removal of minerals was monitored by XRF analysis of recovered Refcoal.

Refcoal recovery and alkali removal

The bulk of the solvent was removed by vacuum distillation at 90 °C. The product was washed with boiling water to remove residual solvent and alkali, and then dried to give Refcoal.

RESULTS AND DISCUSSION

Small-scale extractions

The effect of adding potassium hydroxide (coal:solvent:KOH ratio 10:100:1,6) on the carbon extractabilities into NMP of various South African coals is shown in Table 1. Coals of higher and lower dry, ash-free carbon content showed much lower extractabilities. Clearly the vitrinite concentrates were much more soluble than the corresponding inertinites. Coal B - a flotation concentrate rich in vitrinite - showed a remarkably high extractability considering the mild conditions employed.

The suite of Argonne Premium coal samples [7] was similarly extracted using the same coal:solvent:KOH ratio. The results are given in Table 2 where a similar rank effect is seen. It should be noted that southern African coals have experienced a very different history to those of North America and that direct comparisons based on particular rank parameters should be approached with caution.

The effectiveness of numerous solvents was examined using Coal A and potassium hydroxide in the same ratios as above. The results are given in Table 3. Amide solvents are seen to be generally effective, with dimethyl sulfoxide somewhat less so. Pyridine alone or with KOH was ineffective but the addition of the phase-transfer catalyst 18-crown-6 gave greatly increased extraction when five consecutive extractions were done. Hexamethyl phosphoric triamide was ineffective, even on addition of crown ether.

Various amine, ether, polyether and alcohol solvents showed no great increase in solubility on the addition of potassium hydroxide/crown ether.

Similar results in both NMP and DMF were found when an equivalent amount of sodium hydroxide was used in place of potassium hydroxide. Lithium hydroxide was very much less effective.

The most significant points arising from these results are:

- (1) The organic part of a variety of coals can be very effectively solubilized.
- (2) Relatively cheap and volatile DMF may be used.
- (3) Relatively cheap sodium hydroxide may be used.

Bench-scale extractions

Numerous bench-scale experiments aimed at defining process conditions for the extraction of Coal B have been done using DMF and NMP. The extraction curves found show, in some cases after an induction period, a steadily decreasing rate of extraction until a final plateau is reached.

In summary the more significant observations are:

The effect of air. The extraction is severely affected, with approximately half the potential extraction being obtained.

The effect of temperature. The rate increases rapidly with temperature. In NMP the time to completion ranges from 10 minutes at 180 °C to 17 hours at 30 °C. In DMF the time ranges from 60 minutes at 150 °C to 24 hours at 30 °C. An induction period is seen at lower temperatures.

The effect of alkali. Potassium hydroxide, in equivalent amounts, gives marginally faster extraction.

The form of the sodium hydroxide is important. In NMP and DMF the extraction rate increases with the use of finer NaOH. The induction period becomes shorter. Sodium hydroxide solution gives rapid dissolution, but in DMF the final plateau of extraction is much lower than that found for solid. The addition of more NaOH solution leads to further extraction. Reaction of the base with the solvent must be occurring before the coal is fully solubilized.

The quantity of sodium hydroxide required for maximum extraction in both solvents is about 10% of the mass of the coal.

The effect of phase-transfer catalyst. The addition of as little as 0,7% (of the mass of coal) of polyethyleneglycol 400 increases the rate of extraction noticeably. The addition of 5% polyethyleneglycol 400 decreases the time to maximum extraction at 90 °C in DMF from 200 to 60 minutes. The catalyst clearly assists alkali mass transfer.

The effect of stirring rate. The extraction rate increases with the stirring rate, but plateaus in the bench apparatus at about 1500 r/min.

The effect of particle size. In both NMP and DMF there is a moderate effect at 30 °C and no difference at 90 °C when comparing coals -500 μm +212 μm and -160 μm in size.

Solution properties

The solutions are dark brown in colour. The DMF solution ranges in viscosity from 1,8 cp at 90 °C to 3,5 cp at 30 °C. Solutions in both solvents are unstable when exposed to atmospheric water and carbon dioxide. The NMP solutions have an indefinite stability when in closed containers, but the DMF solutions gel after a few weeks. The addition of acid or other solvents miscible with DMF and NMP leads to immediate precipitation of the coal-derived material.

Monitoring the degree of extraction

The absorption measured correlated extremely well with the degree of carbon extraction determined gravimetrically in a series of partial extractions done in the small-scale extraction apparatus on various coals. The absorbance per gram of coal dissolved remained constant, independent of the degree of extraction for each coal, but differed widely from coal to coal.

Minerals removal

The undissolved coal present in the extraction slurry is highly swollen with solvent and very sticky. Filtration is difficult. Centrifugation at 6000 r/min of the solution directly from the hot extraction vessel gave the best results. Table 4 compares the ash analyses of Coal B with those of a series of unwashed Refcoals prepared from a solution of this coal centrifuged at various speeds. Increased speed is clearly important.

Refcoal recovery and alkali removal

Vacuum distillation of DMF solutions proceeded smoothly at 10 mbar pressure and 90 °C bath temperature, but removal of NMP was difficult and slow. Complete removal of either solvent was not possible but, based on nitrogen analysis, can be brought down to about 10% for DMF and 16% for NMP. Hot-water washing brings these percentages down to < 1% and about 3% respectively. Sodium is also removed by water washing, from 3% in the vacuum-dried product to less than 100 ppm. The final product is a dry, free-flowing granular material. Analysis of Refcoal gave values very close to those found for the coal used in its preparation. Nitrogen increased 0,1 - 0,2%, representing 0,5 - 1,0% DMF, while sulphur was halved, representing removal of pyrite.

Exploitation

Several uses for coal solutions and Refcoal show promise. Refcoal would be a very clean fuel. The carbonization yield of Refcoal prepared from Coal B is 75% at 1100 °C making it an efficient carbon source. Some control of the degree of ordering of the carbon formed appears possible. The low viscosity of the solutions makes it attractive as an impregnation medium. Higher-valued uses are being investigated - fibres can be spun from suitably treated solution and the solution can be used as a source of carbon of high reactivity for the carbothermal preparation of metal carbides and nitrides.

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TABLE 1: Extraction of South-African coals in N-methylpyrrolidone

COAL	% daf C	No additive % carbon extraction	KOH addition % carbon extraction
A	86.8	8.6	80.5
B	88.5	5.0	90.3
C	88.2		80.3
D1 vitrinite	86.8	20.7	47.7
D1 inertinite	86.2	5.4	13.4
D2 vitrinite	87.0	19.0	57.0
D2 inertinite	85.8	6.8	24.8
E1 vitrinite	86.0	10.5	40.0
E1 inertinite	86.3	5.7	16.1
E2 vitrinite	88.8	6.3	86.1
E2 inertinite	86.8	3.4	25.9

TABLE 2: Extraction of Argonne Premium coals into N-methylpyrrolidone/KOH

COAL	% dmmf C	% Carbon extraction
Wyodak-Anderson	76.04	6.0
Beulah Zap	76.05	6.4
Illinois #6	80.73	14.4
Blind Canyon	81.32	16.2
Lewiston-Stockton	85.47	17.5
Pittsburgh #8	84.95	25.3
Pocahantas #3	91.81	76.9
Upper Freeport	88.08	85.8

TABLE 3: Extraction of Coal A in various solvents
(Coal:solvent:KOH ratio 10:100:1,6)

SOLVENT	% CARBON EXTRACTION
N-methylpyrrolidinone	80.5
Dimethylformamide	82.5
Dimethylacetamide	79.4
Tetramethylurea	56.7
Dimethylimidazolidinone	83.1
Dimethyltetrahydropyrimidinone	63.8
Dimethylsulphoxide	62.2
Hexamethylphosphoric triamide	8
Pyridine	6.5 (5 consecutive extractions)
Pyridine + 18-crown-6 + KOH	16.9 (1 extraction)
(70 ml: 0.5 g:0.22 g)	84.5 (5 consecutive extractions)

TABLE 4: A comparison of inorganic elements present in Refcoals prepared from solutions centrifuged at various speeds with their contents in the original coal.

OXIDE	COAL	CENTRIFUGE SPEED (r/min)		
		2000	4000	6000
SiO ₂	4.2%	0.14%	0.11%	0.10%
Al ₂ O ₃	2.1	0.15	0.04	0.03
Fe ₂ O ₃	0.43	0.006	0.01	0.005
CaO	0.28	0.004	-	-
K ₂ O	0.13	0.008	0.004	0.003
TiO ₂	0.18	0.04	0.02	0.015
MgO	0.10	0.03	0.02	0.02
Total	7.4	0.38	0.20	0.17